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ABSTRACT: To enhance the grafting between poly(vinyl alcohol) (PVA) and acrylic monomers at the water/droplet interface, the miniemulsion polymerization approach was investigated. Miniemulsions of *n*-butyl acrylate and methyl methacrylate (50/50 wt %) employing PVA as the stabilizer and hexadecane (HD) as the costabilizer were studied. HD played a critical role in determining the stability of the droplets. Miniemulsions prepared using cetyl alcohol as costabilizer were evaluated in terms of the concentration of cetyl alcohol and the time dependence of the droplet size. These miniemulsions showed a higher rate of degradation due to Ostwald ripening compared to miniemulsions prepared using hexadecane. The droplet size decreased exponentially with increasing PVA, with a lower limit being reached beyond which more PVA had no effect. The PVA partitioning on the surface of droplets was determined by serum extraction using a serum replacement cell. The amount of adsorbed PVA chains on the droplets increased from ~1.0 to ~1.95 mg/m^2 in the range 3−10 wt % PVA and then became constant, as indicated by an increase in the serum concentration of PVA. The trends of the partitioning of PVA on the droplets and the droplet size as a function of PVA concentration were consistent. The sera of miniemulsions prepared with varying MMA/BA compositions were extracted using the serum replacement cell. The amount of serum PVA greatly increased above 75 wt % MMA composition even though the number of droplets increased, indicating that the cross-sectional area of adsorbed PVA molecules on the droplets greatly increased above 75 wt % MMA. The concentration dependence of the grafted PVA on the final particles was similar to that of the number of PVA molecules adsorbed on the monomer droplets, strongly supporting the hypothesis that the water/monomer interface is the main grafting site in the miniemulsion polymerization. The effect of monomer composition on the grafting of PVA was studied. The addition of a small amount of MMA (10−15 wt %) greatly changed the surface characteristics of the final particles and affected the grafting of PVA.

Introduction

The stabilizers used in preparing latexes have a strong influence not only on the colloidal properties of the latex but also on the physical properties of the resulting films. Poly(vinyl alcohol) (PVA)-stabilized latexes show better emulsion fluidity such as Newtonian flow, superior wet primary tackiness as adhesives, good mechanical film properties such as higher tensile strength and creep resistance, excellent mechanical stability, and higher freeze−thaw stability compared to latexes stabilized with low molecular weight surfactants. Nonetheless, the utilization of PVA as a stabilizer in emulsion polymerization has been limited to vinyl acetate systems because it seems to be difficult to graft PVA with monomers such as styrene, butadiene, and acrylic esters.

Generally, there are several routes to obtain grafted PVA. First, grafting can occur by the propagation of PVA macroradicals that are generated by hydrogen abstraction using an initiator. In this reaction scheme, the initiator radical should have the capability of abstracting a hydrogen, and this capability depends on the type of initiator. For example, persulfate initiators such as ammonium persulfate can easily abstract a hydrogen from PVA molecules,[1] and the sites for hydrogen abstraction have been studied using NMR.[2] Okamura and Motoyama studied the effect of initiator type and observed that only 14% of 2,2′-azobis(isobutyronitrile) (AIBN) radicals reacted with PVA, while 97% of ammonium persulfate radicals did.[3] This is probably due to the easier hydrogen abstraction by the sulfate ion free radicals. Meanwhile, after the generation of PVA macroradicals, these radicals should be confined with the monomers in the same location for the grafting reaction to be efficient.

In a second route, grafting can occur by the propagation of PVA macroradicals that are generated by hydrogen abstraction by oligomeric radicals. However, the tendency for hydrogen abstraction by oligomeric radicals of acrylic monomers is much smaller than those of vinyl acetate because of their relatively low reactivity.[4,5] Third, grafting can take place through the termination of the generated PVA macroradicals with the oligomeric radicals. These grafting reactions are limited by the water solubility of the oligomeric radicals. Gilbert described the critical chain length of oligomeric radicals in the aqueous phase for several monomers.[6] If the oligomeric radical surpasses this critical chain length, it will be adsorbed on the preexisting particles or precipitate. This results in a low probability of terminating with PVA macroradicals. From these considerations, the most plausible way to obtain the grafted PVA in acrylic emulsion polymerization seems to be the first approach cited above.

Grafted PVA acts as a polymeric stabilizer on the particle surface. The most effective polymeric stabilizers are considered to be amphipathic block or graft copolymers. The hydrophobic vinyl acetate blocks (or grafts) on the PVA backbone provide the primary anchoring segments, and the hydrophilic vinyl alcohol blocks

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project out into the aqueous phase as stabilizing moieties. In this stabilization mechanism, the grafting architecture seems to be important because the surface activity of polymeric stabilizers is most pronounced when hydrophobic or hydrophilic units are well segregated in the molecule. If the grafted chains are randomly dispersed along the PVA backbone during the polymerization, the stabilization will be poor because there is no clear segregation between hydrophilic and hydrophobic blocks. The grafting architecture for maximum stabilization seems to be in the form of block copolymers, and these can be ideally achieved using functional end groups, which can easily generate radicals by abstracting hydrogen using primary radicals (e.g., hydrogen of −SH end group).

Several researchers have proved that the grafting site is the aqueous phase in conventional emulsion polymerizations,[2,7,8] and hydrogen abstraction mainly takes place at the methine carbons of the PVA.[1,9] In aqueous phase grafting, the hydrogen abstraction by primary radicals on the PVA occurs randomly along the whole chain and is followed by grafting, which may result in a decrease in the stabilization power owing to loss of the boundary of segregation between hydrophobic and hydrophilic portions of the molecule. To maintain the segregation between hydrophobic and hydrophilic portions, the average amount of grafted polymer per PVA molecule should be controlled or the grafted PVA should have a proper grafting architecture such as in block copolymers.

Craig studied the grafting of hydroxyethyl cellulose (HEC) in acrylate emulsion polymerizations and concluded that acrylate monomers (*n*-butyl acrylate was studied) had a higher propensity for grafting to PVA than vinyl acetate because of their higher reactivity, implying that colloidal instability of acrylic emulsion polymer systems stabilized with water-soluble polymers such as HEC and PVA might result from the excessive grafting of the water-soluble polymers (probably a higher amount of grafted polymer per PVA molecule).[10,11] On the basis of this explanation, to maintain the segregation between the hydrophobic and hydrophilic portions by suppressing excessive grafting on the PVA chains in the aqueous phase (actually decreasing the amount of grafted polymer per PVA molecule), several patents have been issued. These patents include the addition of water-soluble regulators such as mercaptoacetic acid and cyclohexylamine,[12] the addition of water-soluble amino alcohol,[13] the combination of water-soluble and oil-soluble initiators such as persulfate initiator and azo type initiators,[14] the modification of PVA with a thiol-terminated group with a specific initiator such as potassium bromate,[15,16] and the addition of alcohol such as methanol.[17,18] Basically, these modifications are based on the suppression of aqueous phase grafting using chain transfer agents, which may result in adverse effects on the reaction kinetics and difficulties in reaction rate control because the addition of water-soluble agents may also affect the concentration of primary radicals. Also, the final particle size was larger (>0.5 μm in most cases) and the distribution broader.

Okaya et al. studied the grafting of PVA in MMA emulsion polymerizations.[19,20] To simulate the early stages of the emulsion polymerization, the monomer concentration was diluted to 1 mL/100 g of water, and 1 g of PVA (DP = 580, DH ~ 88%) was added with various initiator systems such as ammonium persulfate and azo initiators. They found that 90% of the MMA and 60% of the PVA were grafted without any flocculation. Meanwhile, decreasing the PVA to 0.1 g resulted in the formation of coagulum, indicating that the higher amount of PVA is required to stabilize the latex in conventional emulsion polymerization. The amount of grafted PMMA was decreased by adding an alcohol such as isopropyl alcohol, implying that the addition of alcohol actually suppresses the grafting of acrylic monomer on the PVA backbone by decreasing the hydrogen abstraction from PVA by the sulfate radical, because of the competing hydrogen abstraction on the alcohol presumably. Also, it was observed that the particle size became larger with decreasing amount of grafted PMMA by adding alcohol, implying that the system may become unstable. However, there was no information reported on the amount of grafted PVA with added alcohol. Therefore, it is not clear whether the addition of alcohol affects only the amount of grafted PMMA.

Miniemulsions are aqueous dispersions of relatively stable oil droplets with sizes in the 50−500 nm region prepared by shearing a system containing monomer, water, surfactant (stabilizer), and costabilizer, which is added to suppress Ostwald ripening of the droplets.[21] During the formation of a miniemulsion, a large oil/water interface is created, and there will be a large driving force for the adsorption of stabilizer on the monomer droplets. Anderson et al.[22] showed that more than 80% of the sodium lauryl sulfate (SLS) stabilizer was present at the water/droplet interface in styrene miniemulsion systems by determining the aqueous phase SLS concentration via surface tension measurements using the maximum bubble pressure method. Chang et al.[23] determined the critical micelle concentration (cmc) of styrene miniemulsions and macroemulsions stabilized with SLS using a conductance technique. They found that only 10% of the SLS is present at the water/droplet interface in macroemulsions at the cmc, whereas 80% of the SLS is present at the water/droplet interface in miniemulsions at the cmc. Therefore, the miniemulsion technique is an excellent technique to confine the stabilizer at the water/droplet interface. Using the miniemulsion approach, aqueous phase grafting (random grafting presumably) can be minimized, while grafting at the water/monomer interface may still maintain the segregated structure.

In this article, we report, to the best of our knowledge for the first time, the use of poly(vinyl alcohol) as stabilizer in the preparation of acrylic miniemulsions, followed by polymerizations to obtain stable latexes. This article focuses on the study of miniemulsions stabilized with PVA in terms of the type of costabilizer and the concentration of the PVA and then the grafting of PVA in miniemulsion polymerizations as a function of the PVA concentration.

Experimental Section

Materials. *n*-Butyl acrylate (Sigma-Aldrich) and methyl methacrylate (Sigma-Aldrich) were passed twice through an inhibitor-removal column (Sigma-Aldrich). Hexadecane (HD, costabilizer, Sigma-Aldrich), cetyl alcohol (CA, costabilizer, Sigma-Aldrich), sodium bicarbonate ($NaHCO_3$, Fisher), and ammonium persulfate (APS, 99+%, ACS Grade, Sigma-Aldrich) were used as supplied. Poly(vinyl alcohol) (PVA) was obtained as a commercial product (Poval 205, degree of hydrolysis (DH) = 87−89%, degree of polymerization (DP) = 500, Kuraray Co. Ltd., Japan).

Table 1. Recipe for the Miniemulsion Polymerization of *n*-Butyl Acrylate and Methyl Methacrylate

ingredient	weight (g)	concentration
deionized water	80.0	
n-butyl acrylate (BA)[a]	0.0−20.0	
methyl methacrylate (MMA)[a]	0.0−20.0	
PVA 205	0.5−4.0	2.5−20 wt % based on monomer
hexadecane (HD)	0.726	3.6 wt % based on monomer
$NaHCO_3$	0.007	1 mM based on aqueous phase
ammonium persulfate (APS)	0.018	1 mM based on aqueous phase

[a] The weight ratio of total monomers to water always kept at 20/80.

Procedures. a. Miniemulsion Preparation and Polymerization. The recipe used to prepare the various miniemulsions comprising several different formulation components is shown in Table 1. PVA was dissolved by heating at 90 °C for 3 h in deionized water (ca. 6 wt %), and the solution was filtered using a 200 mesh screen. The solids content of the PVA solution was determined gravimetrically and adjusted to 5.9 wt % by adding deionized water.

Miniemulsions Stabilized with HD. A specific amount of HD was mixed with the monomers (BA and MMA). An aqueous PVA solution and DI water were then added to the monomer mixture and stirred for 10 min to prepare a crude emulsion for 10 min prior to subjecting the system to high shear.

Miniemulsions Stabilized with CA. A specific amount of CA was mixed with the PVA solution and DI water and then stirred for 2 h at 70 °C. After cooling, undissolved CA particles were found for the higher amounts of CA (0.833 and 1.744 g). Monomers were added and stirred with a magnetic bar for 24 h to completely dissolve the CA particles and to obtain a good crude emulsion.

The crude emulsions with HD or CA were sonified using a Branson Sonifier (model 450) at a 70% duty cycle and a power setting of 8 for 10 min accompanied by continuous magnetic stirring in an ice bath. All miniemulsion polymerizations were performed in a 500 mL four-neck flask equipped with a reflux condenser, nitrogen gas inlet tube, and Teflon stirrer (~200 rpm) for 24 h at 60 °C.

b. Characterization. Miniemulsion droplet sizes were measured by dynamic light scattering (DLS) (Nicomp, model 370). The emulsion was diluted with a monomer-saturated water solution containing 0.1 wt % PVA. Latex particle sizes were measured by capillary hydrodynamic fractionation (CHDF, model 1100, Matec Applied Sciences) and DLS. The molecular weight of PVA 205 was analyzed at 35 °C by gel permeation chromatography (GPC) using a Waters 515 HPLC pump system with two mixed packed columns (TSK Gel-GMPWXL, Tosohaas) preceded by a guard column (TSK-Gel PWXL). The mobile phase was a 0.01 N $NaNO_3$ solution. Poly(ethylene oxide) polymers with molecular weights from 960 to 730 000 g/mol (Polymer Laboratories, Inc.) were used as the calibration standards. Mark−Houwink constants for poly(ethylene oxide) ($a = 0.66$, $K = 0.488 \times 10^5$) and PVA ($a = 0.64$, $K = 0.428 \times 10^5$) were taken from published values.[24,25] A serum replacement cell was used to determine the partitioning of the PVA between the surface of the miniemulsion droplets and the aqueous phase. Approximately 80 g of a miniemulsion was placed in the cell and confined by a polycarbonate membrane filter having a 0.4 μm pore size. A clear serum phase was withdrawn through the filter. To check the extent of degradation of the monomer droplets during these experiments, the droplet sizes before and after the experiments were compared. The difference between these two values was 2−7 nm, showing a relatively small degradation of the monomer droplets. To obtain enough serum for gravimetric analysis, the serum extraction time was varied from 4 to 16 h depending on the viscosity of the medium.

The amounts of grafted PVA and adsorbed PVA after polymerizations were determined using the selective solubilization process.[26] Separation of the serum from the latex was carried out by ultracentrifugation (Beckman ultracentrifuge, model L8-70M, rotor SW41). Polyallomer (PP copolymer, SETON) centrifuge tubes (9.5 mL) were used with the swinging buckets. Approximately 10 g of original latex (solids contents ~ 20 wt %) was diluted to 10 wt % solids content, stirred for 10 min to achieve a uniform dispersion, and then centrifuged for 12 h at 37 000 rpm and 4 °C. The clear serum was carefully decanted. Acetonitrile was added to disperse and dissolve the sedimented polymer particles that include the grafted PVA and/or the adsorbed PVA and stirred for 7 days via magnetic stirring. Afterward, the residual water was removed by distillation of the acetonitrile/water azeotrope at 76 °C, and then the mixture of acetonitrile and polymers was centrifuged to remove the acetonitrile-soluble polymers, which do not contain grafted PVA or adsorbed PVA (2 h at 18 000 rpm and 4 °C). The supernatant was carefully decanted. The centrifugation was repeated after redispersion of the sedimented polymers until no more polymers were solubilized (3−5 times). The acetonitrile-insoluble polymers that contain both the grafted PVA and PVA adsorbed on the particles were dried, weighed, and mixed with DI water. The mixture was heated to 85 °C and stirred for 24 h to extract the water-soluble polymers (adsorbed PVA). Again, centrifugation was performed to separate the water-soluble polymers and the water-insoluble polymers. The same procedure was repeated once more. The water-soluble polymers were dried and weighed. The amount of grafted PVA was calculated by a total mass balance (grafted PVA = PVA in recipe − PVA in serum of latex − adsorbed PVA). The error was around ±5% for the whole procedure. Any coagulum after polymerizations was screened using a stainless steel mesh (#200) and dried in an oven and weighed.

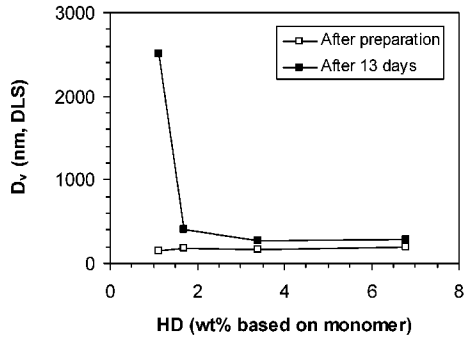

Figure 1. Volume-average droplet diameter of miniemulsions measured by DLS as a function of hexadecane concentration; PVA = 10 wt % based on monomer; BA/MMA = 50/50 wt %.

Results and Discussion

Effects of Costabilizers and Their Concentration on the Miniemulsion Stability. As discussed previously, a stable miniemulsion using PVA and costabilizers should be obtained to enhance the grafting of PVA at the water/monomer interface. Miniemulsion stability was determined by the droplet size as a function of time and concentration of costabilizers (HD and CA) using DLS. Figure 1 shows the effect of HD concentration on the stability of BA/MMA (50/50 wt %) miniemulsions prepared using PVA/HD. The miniemulsion stability was determined by the variation of droplet diameter as a function of time. The initial droplet diameter seemed to be independent of the HD concentration, having an average value of ~200 nm. However, upon aging for 13 days, the droplet diameter greatly increased with decreasing HD concentration, implying instability of the miniemulsion. If the HD concentration was kept above 3.4 wt % based on monomer, the miniemulsion was stable for more than 2 weeks. The stability of various miniemulsions prepared with PVA/

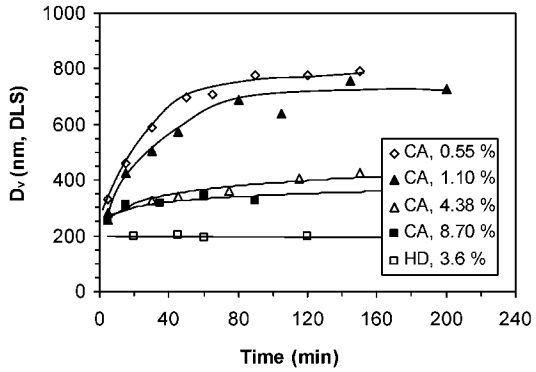

Figure 2. Evolution of volume-average droplet diameter of miniemulsions measured by DLS as a function of cetyl alcohol (CA) concentration; PVA = 10 wt % based on monomer; BA/MMA = 50/50 wt %; lines drawn for visualization purposes only.

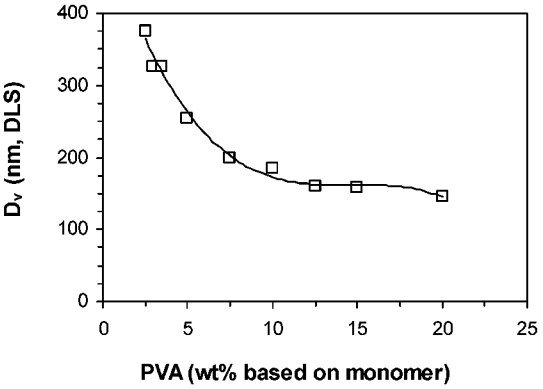

Figure 3. Volume-average droplet diameter of miniemulsions measured by DLS as a function of PVA concentration; BA/MMA = 50/50 wt %; HD = 3.6 wt % based on monomer; line drawn for visualization purposes only.

CA is shown in Figure 2 as a function of time. In contrast to the miniemulsions prepared with PVA/HD, the droplet size increased as soon as sonification was stopped, indicating some instability of the miniemulsions, even with the CA concentration increased to 8.7 wt % based on monomer. Miller[27] studied the stability of toluene miniemulsions prepared with SLS/CA and reported similar results. He pointed out that the primary reason for this instability may result from the redistribution of CA due to its finite water solubility ($\sim 10^{-5}$ g/dm^3), where the slower transport of CA occurs through the aqueous phase, causing a nonequilibrium condition between droplets of different sizes. Therefore, the droplets prepared with CA are easily degraded with time, implying that PVA partitioning at the interface will be decreased with time due to coalescence of droplets and that system is not suitable for our study.

Droplet Size and PVA Partitioning as a Function of PVA Concentration. The effect of the PVA concentration on the droplet size (DLS) in miniemulsions prepared using HD (3.6 wt % based on monomer) as costabilizer is shown in Figure 3. The droplet size decreased exponentially with the PVA concentration and then leveled off, indicating a buildup of PVA molecules in the aqueous phase. To determine the PVA partitioning, the serum PVA of the miniemulsions was collected using a serum replacement cell, and the results are given in Figure 4. As expected from the PVA concentration dependence of the droplet size, the fraction of adsorbed PVA decreased sharply after around

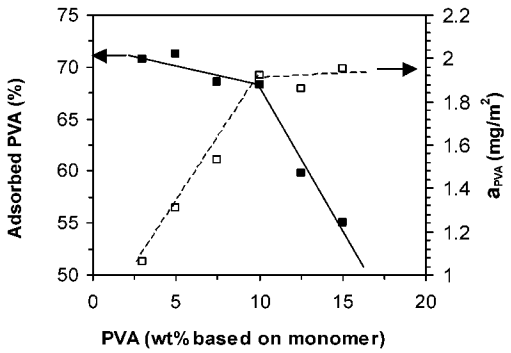

Figure 4. Amount of adsorbed PVA on the droplets as a function of PVA concentration; BA/MMA = 50/50 wt %; HD = 3.6 wt % based on monomer; adsorbed PVA per unit area, a_{PVA}, calculated based on volume-average droplet size; lines drawn for visualization purposes only.

10 wt % PVA. On the basis of the volume-average droplet diameter, the number of adsorbed PVA chains on the droplets increased linearly up to 10 wt % PVA concentration and then was almost independent of the PVA concentration, showing surface saturation. The adsorption of PVA on the droplets at saturation was around 1.95 mg/m^2. Yuki et al. studied the adsorption of PVA on polystyrene (PS) and poly(vinyl acetate) (PVAc) and reported that the amounts of adsorbed PVA at saturation were 3.6 mg/m^2 for PS and 0.5−1.2 mg/m^2 for PVAc and depended on the surface charge density.[15] The difference in the saturation adsorption between MMA/BA miniemulsion droplets (1.95 mg/m^2) and PS (3.6 mg/m^2) or PVAc (0.5−1.2 mg/m^2) can be explained by differences in the hydrophilicity of the surfaces.

From the saturation adsorption ($\sim$1.95 mg/m^2) and degree of polymerization of PVA (DP = 500), the adsorbed area per PVA chain (a_s) was estimated to be 18.8 nm^2 for MMA/BA miniemulsion droplets. The radius of gyration for PVA can be calculated using eq 1:

$$R_g = 4.09(\mathrm{DP}/6)^{1/2} \quad (1)$$

where R_g is the radius of gyration [angstroms] and DP is the degree of polymerization.[28] For the PVA in this study (DP $\sim$ 500, DH $\sim$88%), the projected area ($a_0 = \pi R_g^2$) is about 45.4 nm^2 and the a_s/a_0 ratio $\sim$ 0.414, indicating that the adsorbed PVA chains protrude into the aqueous phase.

Molecular Weight of Serum PVA as a Function of PVA Concentration. Initially, the PVA will have a certain molecular weight distribution as it comes from the manufacturer. There are two scenarios for PVA adsorption on the monomer droplets. Before surface saturation, most of the higher molecular weight PVA molecules will be preferentially adsorbed on the droplets. Therefore, it can be expected that the serum PVA has a lower average molecular weight and somewhat narrower molecular weight distribution compared to the original PVA. After surface saturation, there will be no space for further adsorption of the higher molecular weight PVA, so further addition of PVA will result in its accumulation in the serum including the higher molecular weight PVA. This is expected to increase the average molecular weight of the PVA in the serum and broaden the molecular weight distribution compared to the former case (before surface saturation). Molecular

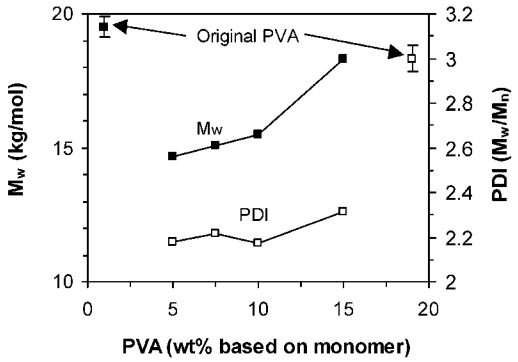

Figure 5. Weight-average molecular weight and polydispersity index of serum PVA as a function of PVA concentration; BA/MMA = 50/50 wt %; HD = 3.6 wt % based on monomer.

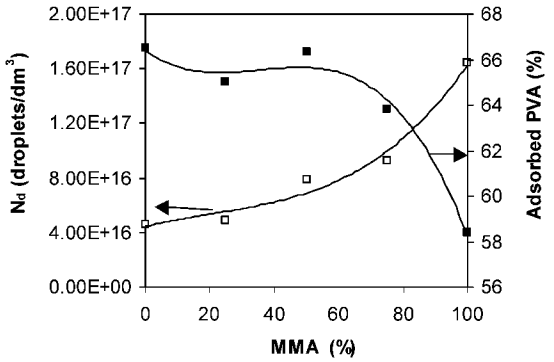

Figure 6. Number of droplets per unit volume and the amount of adsorbed PVA on the droplets as a function of comonomer composition; PVA = 10 wt % based on monomer; HD = 3.6 wt % based on monomer; lines drawn for visualization purposes only.

weights and polydispersity indexes (M_w/M_n) of the serum PVA are shown in Figure 5 as a function of the initial PVA concentration. Values for the original PVA are provided for reference. Basically, the molecular weight and polydispersity of the serum PVA are lower than the original PVA. As expected, the molecular weight in the serum increased sharply and the molecular weight distribution broadened after surface saturation. (As previously discussed, surface saturation occurs around 10 wt % PVA.) However, the molecular weight of the serum PVA after surface saturation was still lower than the molecular weight of the original PVA.

Droplet Size as a Function of Monomer Composition. So far, all miniemulsions were prepared using a fixed comonomer composition (BA/MMA = 50/50 wt %). To further investigate the PVA adsorption on the droplets, the monomer composition was varied for a fixed PVA concentration (10 wt % based on monomer). After the preparation of the miniemulsions, the droplet size at each monomer composition was measured by DLS, and then the serum PVA in the miniemulsion was extracted using the serum replacement cell. The amount of PVA adsorbed on the droplets was calculated by the subtraction of the serum PVA from the original PVA concentration in the aqueous phase. Figure 6 shows the number of droplets per unit volume and the amount of adsorbed PVA as a function of comonomer composition. The number of droplets per unit volume did not change much up to 75 wt % MMA monomer composition. However, a large increase of the number of droplets occurred beyond 75 wt % MMA. From Figure 6, if the cross-sectional area of the PVA molecule adsorbed on the droplets is independent of the comonomer composition, the amount of PVA should increase because the number of droplets per unit volume increased as the MMA composition increased. Therefore, these results show that the cross-sectional area of a PVA molecule greatly depends on the MMA concentration and increases with increasing MMA concentration, especially beyond 75 wt % MMA.

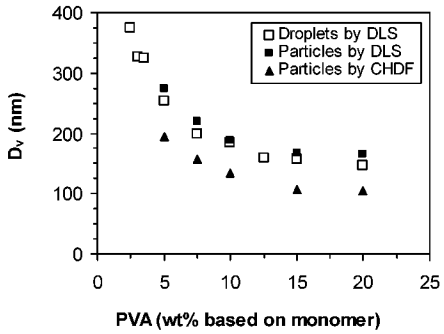

Figure 7. Volume-average droplet diameter measured by DLS and final particle diameter measured by DLS and CHDF as a function of PVA concentration; BA/MMA = 50/50 wt %; HD = 3.6 wt % based on monomer.

Particle Size as a Function of PVA Concentration. Miniemulsion polymerizations were initiated with APS at 60 °C, and stable latexes were obtained. The amounts of coagulum were less than 1 wt % based on monomer. Figure 7 shows the volume-average droplet diameters measured by DLS and final particle diameters measured by DLS and CHDF. To measure the droplet diameters before injection of APS at 60 °C, a small amount of miniemulsion was withdrawn from the reactor and cooled, and then the droplet size was measured by DLS as a function of the PVA concentration. The final particle diameter measured by CHDF at each PVA concentration was smaller than that measured by DLS; however, the PVA concentration dependence of the final particle diameter measured by CHDF was similar to that measured by DLS. The PVA concentration dependence of the final particle diameter measured by DLS was similar to that of the droplet diameter; the final particle diameter is close to the droplet diameter at each PVA concentration, implying that droplet nucleation may be predominant, and most of the initial droplets were nucleated.

Grafted and Adsorbed PVA of Latexes as a Function of PVA Concentration. The selective solubilization method was employed to separate the serum, grafted, and adsorbed PVA in the final latex. Figure 8 presents the amounts of grafted and adsorbed PVA as a function of PVA concentration based on a unit surface area. The amount of grafted PVA per unit area continuously increased up to 10 wt % PVA and then became constant, which is consistent with the PVA concentration dependence of adsorbed PVA on the miniemulsion droplets. This strongly supports the hypothesis that the water/monomer interface is the main grafting site in the miniemulsion system.

Evolution of Number of Particles (N_p) as a Function of Monomer Composition. The preceding polymerizations were performed at a fixed comonomer composition (BA/MMA = 50/50 wt %). To further investigate the PVA grafting reaction in terms of monomer composition, the monomer composition was varied for a fixed PVA concentration (10 wt % based on monomer). Basically, all polymerizations carried out were stable for 24 h at 60 °C (coagulum < 0.5 wt %

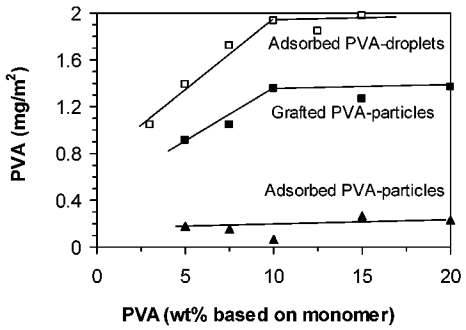

Figure 8. Amount of PVA grafted and adsorbed per unit area of the final particles (obtained using the selective solubilization method) and the amount of PVA adsorbed on the droplets as a function of the PVA concentration (obtained via a serum replacement cell); PVA = 10 wt % based on monomer; HD = 3.6 wt % based on monomer; amount of PVA adsorbed on the droplets was estimated based on the volume-average droplet diameter measured by DLS; amounts of PVA grafted and adsorbed on the particles were estimated based on the volume-average particle diameter measured by CHDF; lines drawn for visualization purposes only.

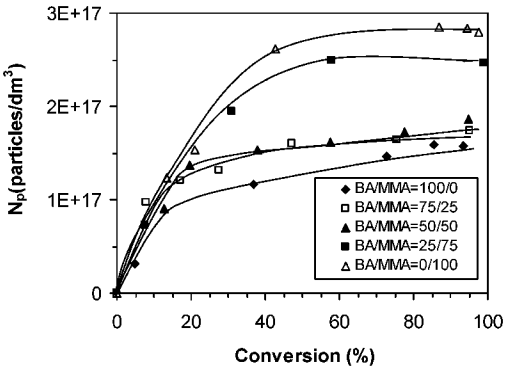

Figure 9. Number of particles per unit volume of aqueous phase as a function of comonomer composition and conversion; PVA = 10 wt % based on monomer; HD = 3.6 wt % based on monomer; particle size (D_v) was measured by CHDF; lines drawn for visualization purposes only.

based on monomer). Figure 9 shows the evolution of the number of particles (calculated from the volume-average particle diameters measured by CHDF) during the polymerization as a function of monomer composition. Particle nucleation seems to cease at around 60% conversion, and the nucleation mechanism does not appear to differ much for each composition. The final number of particles increased with increasing MMA in the comonomer. However, the increase of the final number of particles is larger beyond 75 wt % MMA, which is consistent with the composition dependence of the initial number of monomer droplets, implying that droplet nucleation is operative primarily.

Serum of Latexes as a Function of Monomer Composition. The latex serum was extracted by two techniques, filtration (using a serum replacement cell (SRC)) and ultracentrifugation (UC), and compared with the original emulsion serum (Figure 10). The original latex was diluted to ~10 wt % solids for an efficient separation of the serum by ultracentrifugation. There was a small difference (~2%) in the two methods; however, the trend was the same. For homopolymers such as PMMA and PBA or copolymers with low MMA contents (<10%), the amount of serum PVA in the latexes was similar to that in the emulsions, implying little desorption during the polymerization. However, for the copolymers with high MMA content (>10 wt %),

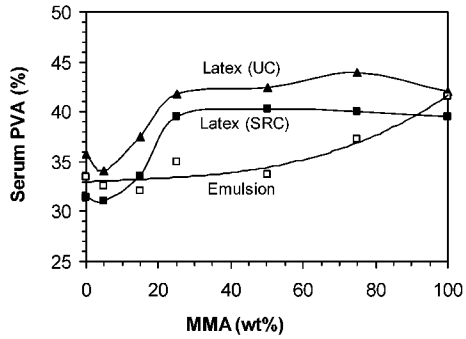

Figure 10. Amount of serum PVA in latexes and miniemulsions as a function of monomer composition; UC = ultracentrifugation, diluted to ~10 wt % solids content; SRC = the serum replacement cell, ~20 wt % (original solids content); lines drawn for visualization purposes only.

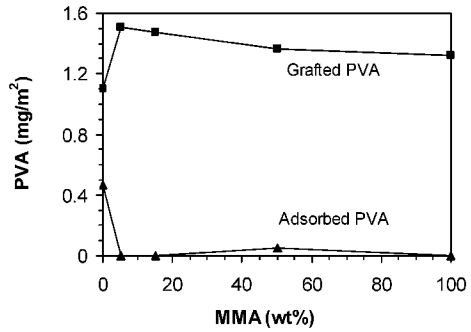

Figure 11. Amounts of grafted and adsorbed PVA per unit area of the final particles as a function of MMA concentration obtained using the selective solubilization method; PVA = 10 wt % based on monomer; HD = 3.6 wt % based on monomer; amounts of PVA grafted and adsorbed on the particles were estimated based on the volume-average particle diameters measured by CHDF.

the amount of serum PVA in the latexes was always larger than that in the corresponding miniemulsions, indicating a relatively significant desorption of PVA molecules during the polymerization. As previously discussed, the behavior of the amount of serum PVA in miniemulsions and the number of droplets per unit volume (N_d) were similar up to 75 wt % MMA, which means that the droplet surface characteristics do not differ much as a function of MMA up to 75 wt % MMA. In contrast, the addition of a small amount of MMA (10−15 wt %) greatly increased the PVA desorption during the polymerization. However, further additions of MMA did not result in a further increase in PVA desorption, suggesting that the surface characteristics of the final polymer particles abruptly change beyond 10−15 wt % of MMA in the monomer mixture.

Grafted PVA as a Function of Monomer Composition. Figure 11 shows the amounts of adsorbed and grafted PVA in the final latexes as a function of the monomer composition. The amount of grafted PVA per unit area decreased as the addition of MMA increased from 5 wt % MMA. This might result from the decrease in the adsorbed PVA per unit area during the polymerization due to the changed surface characteristics, indicating again that the grafting depends on the number of adsorbed PVA molecules on the droplets/particles. The addition of a small amount of MMA (5 wt %) greatly increased the grafting, and this suggests that some portion of the grafting may actually occur in the aqueous phase.

Conclusions

Miniemulsions of *n*-butyl acrylate and methyl methacrylate (50/50 wt %) employing poly(vinyl alcohol) (PVA) as the sole stabilizer and hexadecane (HD) as the costabilizer were studied. HD played a critical role in determining the stability of the miniemulsion droplets, and 1.85−2.78 wt % of HD based on the monomers was required to obtain relatively stable droplets. The droplet size decreased exponentially as the concentration of PVA was increased, reaching a lower limit. The number of adsorbed PVA chains on the droplets increased as the PVA concentration in the system increased up to around 10 wt % and then remained almost constant, indicating droplet surface saturation. A comparison of the number of droplets and the amount of the serum PVA in the miniemulsions showed that the cross-sectional area of the adsorbed PVA molecules on the droplets greatly increased above 75 wt % MMA in monomer composition. The concentration dependence of grafted PVA was similar to that of the number of PVA molecules adsorbed on the monomer droplets, strongly supporting the hypothesis that the water/monomer interface is the main grafting site in these miniemulsion polymerizations. Increasing MMA in the monomer composition had a great influence on the surface characteristics of the final particles, which caused a decrease in the amount of adsorbed PVA during the polymerization and resulted in a decrease in the amount of grafted PVA per unit area.

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